
Impact of Manure Placement on Nitrogen and Phosphorus in Simulated Snowmelt Runoff From a Soil in East-Central Saskatchewan

Tom King¹ and Jeff J. Schoenau¹

¹Department of Soil Science, University of Saskatchewan, Saskatoon, SK S7N-5A8

Key Words: solid cattle manure, subsurface injection, soil nitrate-nitrogen, soil phosphorus, dissolved organic carbon, total nitrogen

1. Introduction

The expansion of the intensive livestock industry in western Canada has lead to subsequent concerns about the overloading of nitrogen (N) and phosphorus (P) nutrients in soil. In areas that receive high application rates of animal manures, elevated transport of particulate and dissolved P and N by water can be of concern in soils that are overloaded in nutrient (Carefoot and Whalen, 2003; Lee et al., 2003). For example, since the 1990's soil P levels in Manitoba have increased due to manure application and agricultural sources have been identified as responsible for supplying 15% of Manitoba's portion of the P loading into Lake Winnipeg (Barker, 2007).

Solid cattle manure can be high in N and P and there is potential for movement of the various forms of organic and inorganic N and P from the field, leading to adverse nutrient enrichment of surface and subsurface water bodies. This in turn can lead to health effects in humans such as methemoglobinemia from consuming water that is high in nitrate-nitrogen. High P levels in water bodies can lead to eutrophication and the growth of algae which restricts oxygen supplies for other marine and plant growth.

Organic forms of P that dominate in many manure sources are important in the bioavailability of soil P. However, the specific composition of soil P pools and their turnover and mobility are not well understood. Animal manure that is applied to soil differs in the forms and concentrations of P and N as related to animal species, housing, feed, operations, handling and storage of manure. In runoff or leachate water from soils, there can be four categories of P forms including 1) dissolved reactive P (soluble orthophosphate), 2) particulate reactive P (insoluble total P fraction adsorbed on clay, iron, aluminum or clay oxides), 3) dissolved unreactive P (primarily organic P compounds) and 4) particulate unreactive P in which the nature of the P compounds could be sorbed P on mineral humic acid complexes (Toor et al., 2006). The movement of P from cultivated fields has been reported to occur mainly through the subsurface via matrix flow and preferential flow (Gachter et al. 1998; Simard et al. 2000).

Consideration of the forms and distribution of N and P in Saskatchewan agricultural soils as affected by manure management practices is the first step in assessing the potential influence of the practice on potential for nutrient migration. Soil will retain a majority of the P and N applied as animal manure that is not removed by the crop through transformations such as immobilization, adsorption and precipitation. Soil characteristics control the forms in which P is transported from the bulk soil to surface or underground water systems (Ulen and Snall, 2007). The P mobility is strongly controlled by its chemical and physical form (Hountin et al., 2000).

Manure application method such as broadcasting and incorporation or subsurface injection of manure could have effects on the amount, distribution and forms of N and P in the leachate that is carried off a field.. The objective of this research was to examine N and P forms and mobility as affected by different application methods of solid cattle manure (SCM). Specifically, intact thin sections of surface soil collected from field application treatments and exposed to simulated snow melt run off were used to determine how manure application potentially affects N and P in run-off.

2. MATERIALS AND METHODS

2.1 General Experimental Setup

The SCM field trial was set up as a randomized complete block design. Treatments were replicated four times at Dixon. The Dixon site was established in the spring of 2007 when SCM was applied to the plots. There are two control plots for the SCM trial at Dixon, the first consisting of no manure or fertilizer being applied and no disturbance of the soil, the second control plot consisting of no manure or fertilizer being applied and disturbance of the soil using the coulter openers of the SCM injector machine.

Solid cattle manure was applied using four application procedures; 1) broadcast application where SCM is applied on the soil surface (no incorporation), 2) broadcast and incorporated where SCM is applied on the soil surface and then incorporated using a disk, 3) subsurface injection, where SCM is subsurface injected using the PAMI Solid Cattle Manure Injector Machine in six subsurface trenches by 24 inch coulter openers spaced 30 cm apart applying SCM product 10-13 cm in depth. Eighteen inch closing wheels cover the exposed injection trench with soil, 4) commercial urea fertilizer (46-0-0) is banded into the soil using a small plot drill prior to the injection of the SCM. Rate of urea fertilizer application is 78 kg N ha^{-1}) After the banding of the urea fertilizer, SCM is subsurface injected as described above.

The lowest rate of SCM being applied (1X) was equal to $100 \text{ kg total N ha}^{-1}$, at a rate of $20.2 \text{ tonnes ha}^{-1}$, and may be considered an agronomic rate in line with the amount of N that would be recommended as fertilizer manure to meet a crop requirement. Higher rates of SCM (2X = $40.4 \text{ tonnes ha}^{-1}$, 3X = $60.6 \text{ tonnes ha}^{-1}$) were considered to be

double and triple the recommended agronomic rates of N fertilizer application for an application made every year.

2.2 Site Description

The SCM injection study at Dixon was established in the spring of 2007 before spring seeding operations commenced with the first applications of SCM. The experiments were initiated on the southern half of a farm field (legal location NW 21-37-23-W2) located approximately 6.5 km west of the town of Humboldt adjacent to Saskatchewan Provincial Highway #5, within the Rural Municipality of Humboldt (Figure 3.1). The soil at this site belongs to the Cudworth Association and is a Black Chernozemic soil formed in calcareous, silty, lacustrine parent materials and having a loam surface texture (Saskatchewan Soil Survey, 1989). Crops grown on the Dixon site were oats in 2007 and canola in 2008.

2.3. Experimental Design

The SCM injection trials at the Dixon site consisted of 14 treatments that were each replicated in four blocks, arranged in west to east direction. All treatments in were laid down in a randomized pattern in the spring of 2007 before the producer commenced seeding operations. The plot size of the SCM trial are 6.09 m by 6.09 m. The treatments in the SCM trials are listed in Table 2.1.

Table 2.1 Treatments in the solid cattle manure trials that were sampled for the thin section run-off study at the Dixon site.

Treatment†	Sequence	N rate	Application method
0 T ha ⁻¹	control-disturbed	0 kg N ha ⁻¹	with no incorporation, but disturbance
60.6 T ha ⁻¹	4X	400 kg N ha ⁻¹	cattle manure broadcast only
60.6 T ha ⁻¹	4X	400 kg N ha ⁻¹	cattle manure broadcast and incorporated
60.6 T ha ⁻¹	4X	400 kg N ha ⁻¹	cattle manure subsurface injected
60.6 T ha ⁻¹	4X+U	400 kg N ha ⁻¹	cattle manure subsurface injected + urea
urea fertilizer	U	78 kg N ha ⁻¹	banded urea 46-0-0 fertilizer

† Application rate based on wet weight.

2.4 Manure Applications

The SCM applied in the field trial at Dixon was obtained from the Poundmaker Feedlot, which is located approximately 8 km east of the town of Lanigan, SK. The manure was applied to the appropriate plots using the PAMI Solid Cattle Manure Injector Machine mixture. Application rates of the SCM are listed in Table 3.1. The SCM was applied to the Dixon site on June 12 and 13, 2007 for the 2007 crop year. The SCM was applied to the Dixon site on May 10, 2008 for the 2008 crop year.

2.5 Field Soil Sampling

Thin sections, as intact blocks of surface soil, were collected from designated plots at Dixon in October 2007 after harvest operations had concluded for that crop year. In each designated plot, a small trench was excavated to expose a 30 cm by 50 cm section of soil. A crosscut hand saw was used to cut the 30 cm by 50 cm soil section at an approximate depth of 5-10 cm. Once the thin section had been severed, a plastic sheet was inserted into the severed section in order to remove the thin section as intact as possible taking care not to fracture the 30 cm by 50 cm thin section in separate fragments. The thin section was placed in a plastic storage container for transportation back to the University of Saskatchewan for storage at -20 °C. The thin section consisted of the upper 5-10 cm of soil plus the accompanying crop residues.

Soil samples from designated plots were taken using polyvinylchloride (PVC) pipes measuring 15 cm in height and 10 cm in diameter. Four PVC cores were inserted per designated sampling plot. The 0-15 cm depth was sampled. The PVC cores were inserted by setting the cores on the soil surface and pushing them into the soil. The cores were then removed by excavation, bagged, labeled, removed from the site and transported to the University of Saskatchewan for storage at -20 °C for processing.

2.6 Determination of Nitrogen and Phosphorus in Soil Thin Section Runoff

The soil thin section monoliths were placed inside insulated plywood boxes designed to slow the rapid thawing of the soil thin section so as to allow the added snowcover to infiltrate the subsurface of the soil and not just run off the soil surface. Approximately 2 kg of snow representing about 7.5 cm of snow cover in a field were added to the thin section surface. The rear of the insulated plywood boxes was elevated to a position of 5 degrees to allow leachate runoff to occur. The boxes were lined with plastic sheets directing snowmelt leachate to be collected in a plastic bucket. The leachate was collected in plastic buckets, volume collected measured and recorded and stored at -20 °C until samples were filtered using Millipore 45 µm glass filters. The filtered samples were analyzed for ammonium, nitrate and phosphate using automated colorimetry.

2.7 Determination of Nitrogen and Phosphorus in Intact Soil Core Runoff

The bottoms of intact soil cores were covered with cheesecloth to keep the soil intact in the core. Collection dishes were placed underneath the cores to collect leachate. Soil field capacity was determined and cores were wetted to approximate field capacity. Approximately 200 ml of distilled water was added to each core and allowed to equilibrate for 48 h. Water that leached through the soil cores during this period was collected and poured back onto the cores to maintain field capacity.

Two separate leaching operations were conducted. In each leaching event, the intact soil cores were leached with 392ml of distilled water calculated by the volume of the cylinder (10 cm diameter, 15 cm height), using the following formula:

Volume of leachate water:

$$\text{Pi}/4 \times (\text{cd}) \times \text{h} \quad [\text{Eq 1}]$$

Where $\text{Pi} = 22/7 = 3.142857143$

cd = core diameter (cm)

h = height of core (cm)

All leachate water was collected and the volume of the leachate was recorded. The leachate water was stored in a freezer at -20°C until samples were filtered using milipore $45\ \mu\text{m}$ glass filters. The filtered samples were then analyzed for ammonium, nitrate and orthophosphate using a Technicon™ automated colorimetry analyzer.

3. Results and Discussion

3.1 Spring 2008 Soil Samples

Soil samples were obtained from the control treatment, broadcast 3X treatment, broadcast and incorporated 3X treatment and injected 3X treatment plots at the Dixon SCM site in the spring of 2008. These samples were sectioned into 0-5, 5-10 and 10-15 cm depths and each depth was analyzed for $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$ and P. Soil $\text{NO}_3\text{-N}$ was slightly higher for all three depths in the three SCM treatments versus the control treatment (Figure 3.1). There was no significant differences ($p < 0.10$) in soil $\text{NO}_3\text{-N}$ between the three SCM treatments for all three depths. The broadcast 3X 0-5 cm and injected 3X 5-10 cm depth were found to have the highest amount of soil $\text{NO}_3\text{-N}$ ($7.3\ \mu\text{g g}^{-1}$).

Broadcast SCM would have more organic matter located at the soil surface, unlike the injected treatment. The injected 3X treatment is solid cattle manure applied in bands and applied at a 8-10 cm depth, so it would be expected that more $\text{NO}_3\text{-N}$ would be found at this depth due to decomposition of the manure. Over time more of the SCM would be decomposed by soil microbes converting organic N into inorganic N.

There were no significant ($p < 0.10$) differences found in the soil $\text{NH}_4\text{-N}$ for all four treatments at the Dixon SCM injected site (Figure 3.2). Soil $\text{NH}_4\text{-N}$ averaged around $7 \mu\text{g g}^{-1}$ across all three depths all four treatments. The highest $\text{NH}_4\text{-N}$ was found in the broadcast 3X 0-5 cm treatment, although this was not significantly different ($p < 0.10$) from the other 0-5 cm depths of the other three treatments.

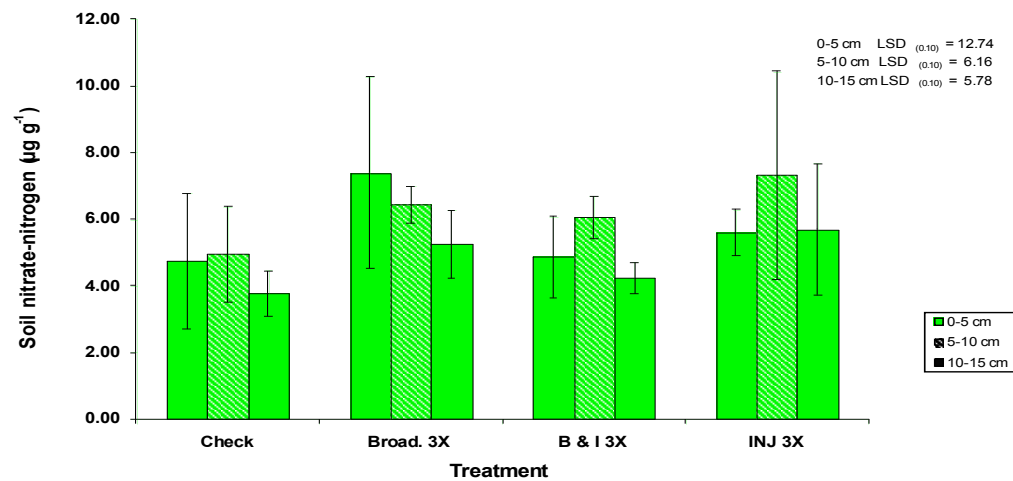


Figure 3.1 Dixon SCM site soil nitrate-nitrogen at 0-5, 5-10 and 10-15 cm depth spring 2008.

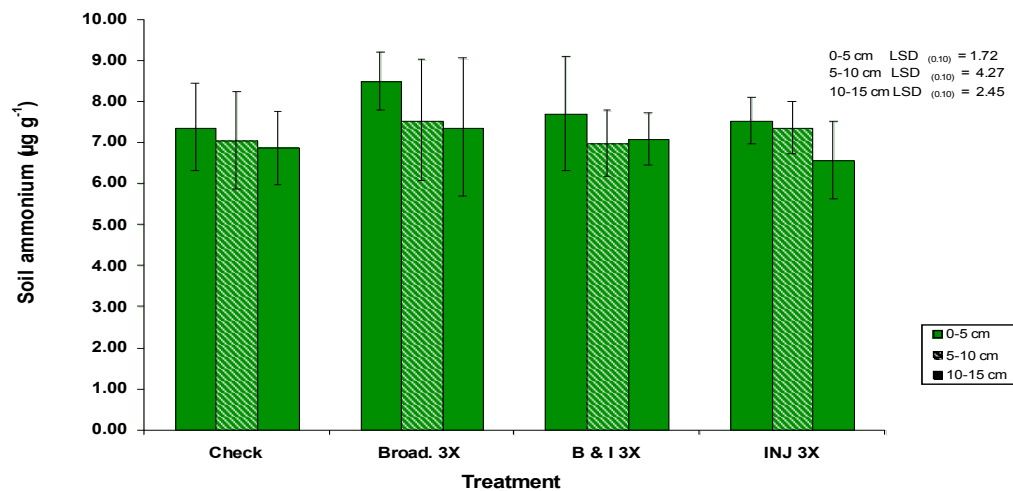


Figure 3.2 Dixon SCM site soil ammonium at 0-5, 5-10 and 10-15 cm depth spring 2008.

Soil extractable (Modified Kelowna) P levels in the three manured treatments were found to be significantly different ($p < 0.10$) in the 0-5 cm depth versus the control (Figure 3.3). Soil extractable P was highest in the broadcast 3X treatment ($245 \mu\text{g g}^{-1}$) and decreased to just over $160 \mu\text{g g}^{-1}$ in the broadcast and incorporated 3X and injected 3X treatments for the 0-5 cm depth. Soil extractable P decreased to just over $40 \mu\text{g g}^{-1}$ for the broadcast and broadcast and incorporated treatments at the 5-10 cm depth, however, the injected 3X 5-10 cm depth showed a P level of $123.0 \mu\text{g g}^{-1}$, which was significantly ($p < 0.10$) higher than the other three treatments (Figure 3.3). This is the depth at which the SCM is injected in a band. More soil P was measured at the 0-5 cm surface soil depth for all three manure treatments compared to the control. Surface placement of cattle manure results in the greatest nutrient stratification, with highest concentration at the surface that decreased more rapidly with depth.

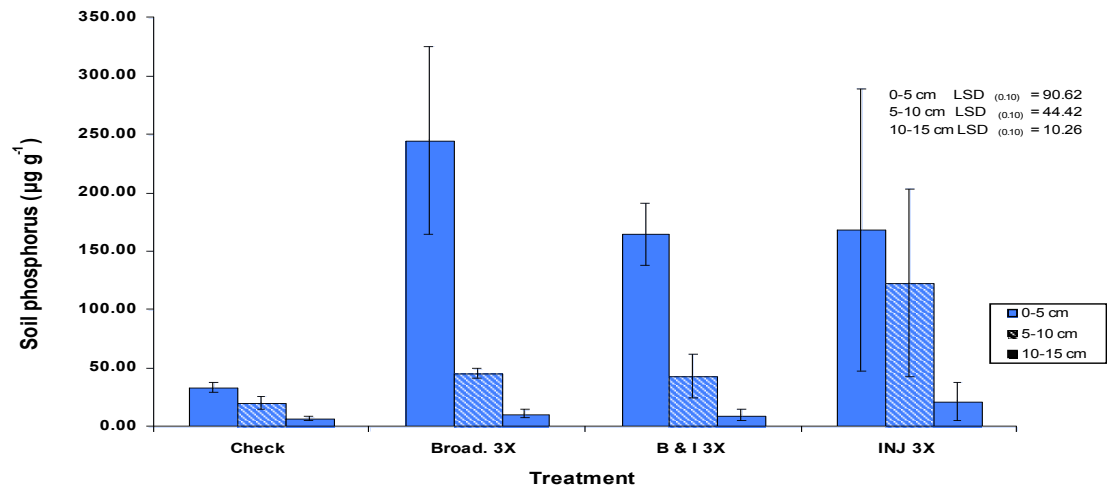


Figure 3.3 Dixon SCM site soil extractable phosphorus at 0-5, 5-10 and 10-15 cm depth spring 2008.

The injected 3X treatment showed higher levels of $\text{NO}_3\text{-N}$ and extractable P at the 5-10 cm depth than the broadcast 3X and broadcast and incorporated 3X treatments. This is the result of the manure being directly placed in a band at approximately 8-10 cm depth and the organic material undergoing decomposition by soil microbes to release nutrients via mineralization. The broadcast and incorporated 3X treatment would have some of its manure mixed under the soil surface with the incorporation. However, not all of that particular treatment manure would get mixed into the soil subsurface. There would be some material that is mixed with the soil at a shallower depth. Surface placement without incorporating or shallow incorporation would be expected to reduce the rate of decomposition and release of soluble inorganic ions due to drier soil conditions that are less favorable for decomposition.

3.2 Dixon Solid Cattle Manure Injection Site Soil Thin Section Run-Off

Thin section soil monoliths were excavated in the fall of 2007 to examine the effect that simulated snowmelting conditions imposed in a laboratory would have on the composition of the runoff/leachate being collected. Thin sections that had snow applied and the resulting runoff/leachate collected were measured for total organic carbon (TOC), total N (TN), $\text{NO}_3\text{-N}$ and orthophosphate (P). Total organic carbon measured in runoff/leachate from the soil thin sections showed that those monoliths obtained from injected 3X treatment plots had significantly ($p < 0.10$) higher TOC concentrations than the other two manured treatments (Figure 3.4). Total organic carbon was measured at 44.8 kg ha^{-1} in water runoff/leachate samples collected from snowmelt in the injected 3X treatment soil thin sections. This was significantly ($p < 0.10$) higher than the 18.9 and 16.8 kg ha^{-1} measured in the broadcast 3X and broadcast and incorporated 3X, respectively, treatments.

Total N in runoff/leachate collected from the injected 3X treatment was equivalent to 5.2 kg ha^{-1} , which was significantly ($p < 0.10$) higher than the 2.8 and 2.1 kg ha^{-1} in the broadcast 3X and broadcast and incorporated 3X, respectively, treatments (Figure 3.5). The measured TN in all three manure treatments shows the same pattern as the TOC for all three manured treatments. The snowmelt water runoff/leachate samples collected from simulated snowmelt suggests that injected SCM will result in greater export of TN and TOC in sub-surface water flow during snowmelt. This may be explained by the movement of water through the thawed subsurface region of the monolith as the soil thawed from the surface downwards during the snowmelt runoff. Water that passes through the 5-10 cm layer with greater concentration of soluble nutrients would be expected to transport more nutrients. Therefore, although injection of SCM is anticipated to reduce surface runoff when the surface of the soil is frozen as it is in early spring, it may increase export through subsurface water movement that may occur with snowmelt or rain received later in the spring on unfrozen soil.

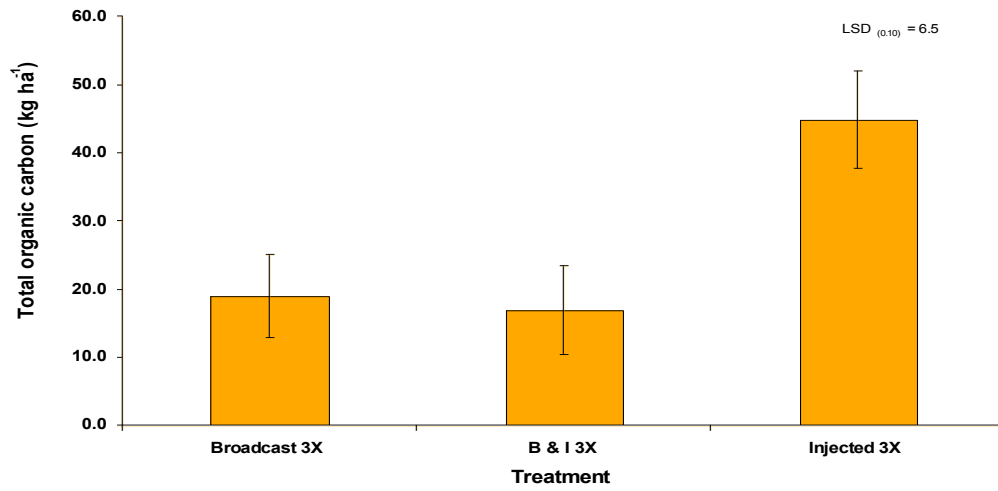


Figure 3.4 Dixon SCM site thin section monolith snowmelt total organic carbon.

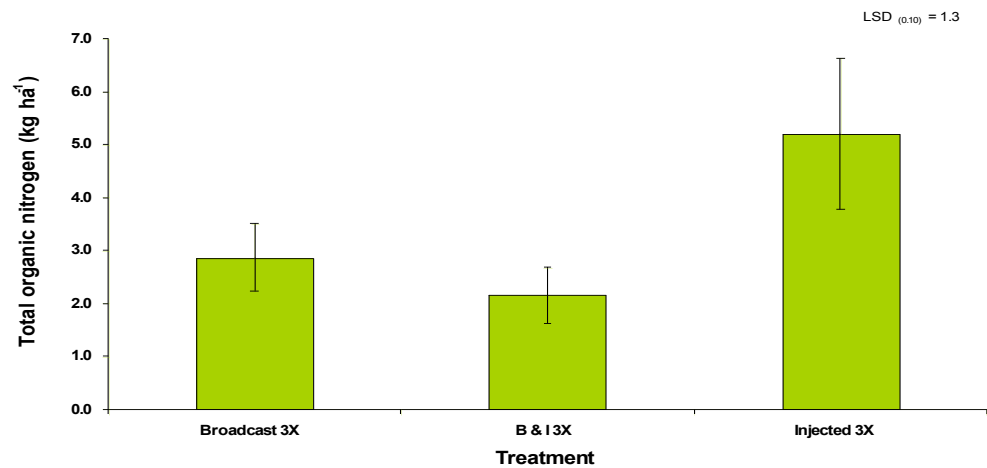


Figure 3.5 Dixon SCM site thin section monolith snowmelt total nitrogen.

Thin section snowmelt runoff/leachate was also measured for NO₃-N and P. The NO₃-N for the injected 3X and broadcast and incorporated 3X manure treatments was found to be 5.6 and 6.5 kg ha⁻¹, respectively (Figure 3.6). Both of these treatments had nitrate export from the thin sections that was significantly ($p < 0.10$) higher than the 0.7 kg ha⁻¹ measured in the broadcast 3X treatment (Figure 3.6).

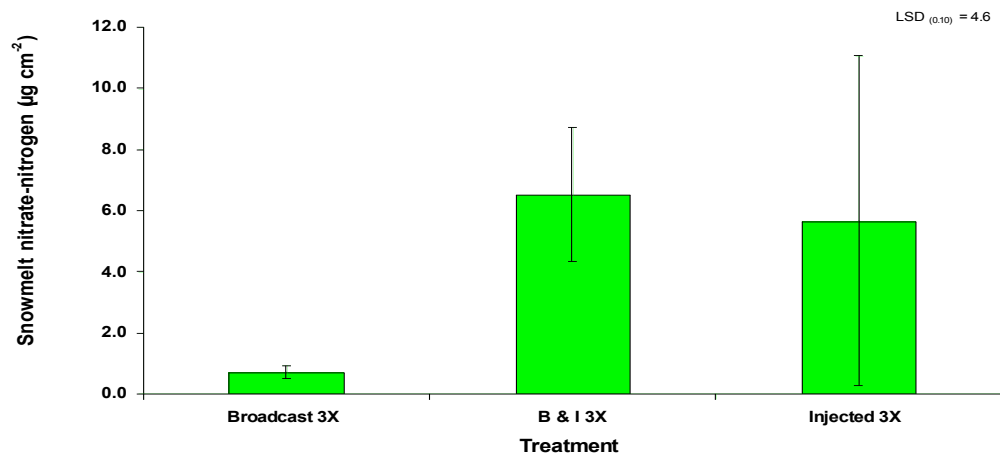


Figure 3.6 Dixon SCM site thin section monolith laboratory snowmelt leachate nitrate-nitrogen.

Snowmelt leachate was also analyzed for orthophosphate and the injected 3X manure treatment was found to be higher (although not significantly) in P (6.0 kg ha⁻¹) than the broadcast 3X and broadcast and incorporated 3X manure treatments runoff/leachate (Figure 3.7).

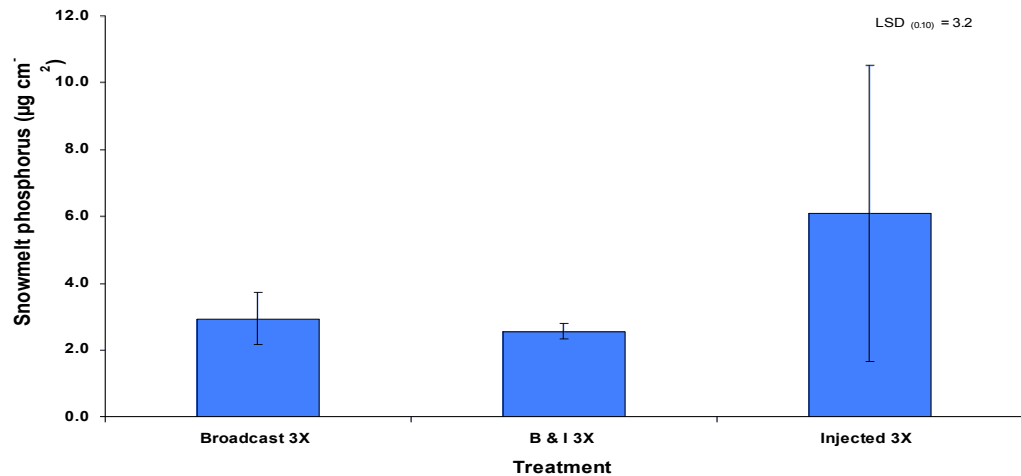


Figure 3.7 Dixon SCM site thin section monolith laboratory snowmelt leachate phosphorus.

The fact that the TN, TOC, nitrate and orthophosphate was higher in the injected 3X manure treatment than the broadcast 3X and broadcast and incorporated 3X treatments suggests that the movement of these constituents may be accentuated by placement at depth in bands when sub-surface flow occurs on un-frozen soils. The observation that broadcast SCM is not showing higher levels in runoff/leachate may be a result of the greater prevalence and importance of the subsurface flow, rather than over the surface of the soil during snowmelt in this simulation. Manure placed at depth may decompose more rapidly to release soluble nutrient that is subsequently carried laterally by subsurface flow. Injection channels may also provide a conduit for water flow. Field work is required to validate these findings.

3.3 Dixon Solid Cattle Manure Injection Site Intact Soil Cores

Intact soil cores measuring 15 cm in depth and 10 cm in diameter were collected in the fall of 2007 to examine the effect that simulated water leaching conditions imposed in a laboratory would have on the composition of the leachate that makes its way through the surface layer of the soil. Soil cores that had water applied and the resulting leachate collected were measured for total organic carbon (TOC), total N (TN), $\text{NO}_3\text{-N}$ and orthophosphate (P). Total organic carbon measured on intact soil cores showed that those cores from injected 3X treatment plots had higher TOC levels than the other two manured treatments (Figure 3.8).

The results are in agreement with the snowmelt monolith runoff/leachate experiment described in the previous section. Total organic carbon was measured to be $13.5 \mu\text{g g}^{-1}$ in water leachate samples collected from injected 3X treatment core. This was higher than the leachate TOC of 6.4 and $7.6 \mu\text{g g}^{-1}$ in the broadcast 3X and broadcast and incorporated 3X, respectively, treatments. During a second leaching, the injected 3X treatment was also found to have higher levels of TOC than either the broadcast 3X and broadcast and incorporated 3X treatments (Figure 3.8).

Total N for both the first and second leaching of the intact soil cores for the injected 3X treatment was measured at 3.5 and $1.9 \mu\text{g g}^{-1}$, respectively, which was higher than the 2.8 and $1.7 \mu\text{g g}^{-1}$, in the broadcast 3X and broadcast and incorporated 3X, respectively, treatments (Figure 3.9).

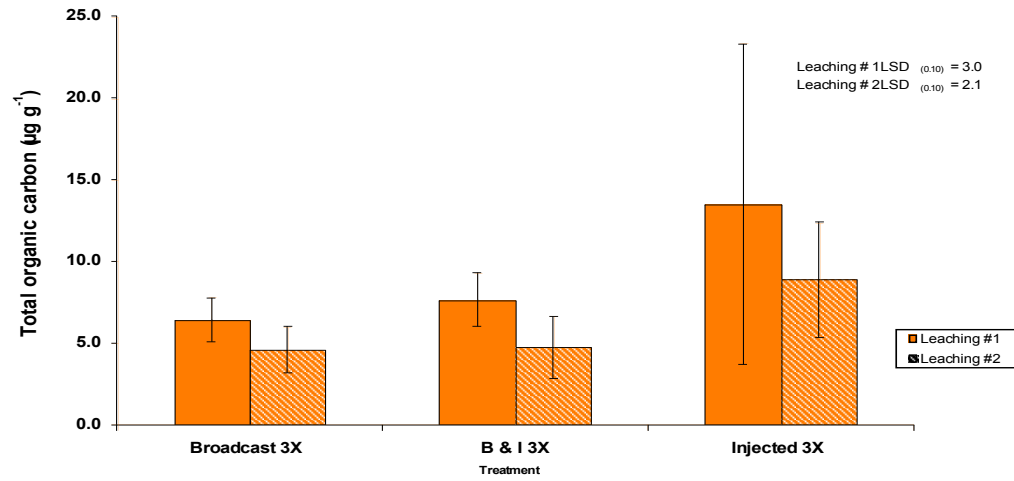


Figure 3.8 Dixon SCM site intact 0-15 cm depth soil cores leachate total organic carbon.

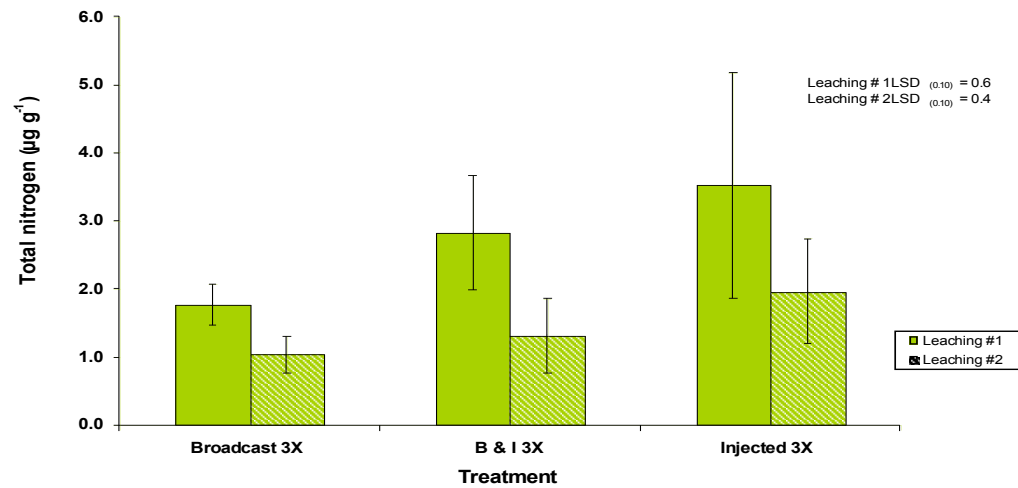


Figure 3.9 Dixon SCM site intact 0-15 cm depth soil cores leachate total nitrogen.

The measured TN in all three manure treatment soil cores shows the same pattern as the TOC for all three manured treatments. The water leachate samples suggests that injected SCM will result in more TN and TOC movement by water flow through the soil matrix versus the other two manure treatments.

The leachate from the intact soil core was measured for $\text{NO}_3\text{-N}$ and P. The leachate $\text{NO}_3\text{-N}$ from the first leaching for the injected 3X and broadcast and incorporated 3X manure treatments was measured at 0.93 and 0.92 kg ha^{-1} , respectively (Figure 3.10). Both of these treatments revealed a greater amount of $\text{NO}_3\text{-N}$ in the first leaching than the 0.56 kg ha^{-1} measured in the broadcast 3X treatment (Figure 3.10). Leachate $\text{NO}_3\text{-N}$ from the second water leaching for the injected 3X and broadcast and incorporated 3X manure treatments was measured at 0.33 and 0.31 kg ha^{-1} , respectively and was double the 0.15 measured in the broadcast 3X treatment (Figure 3.10).

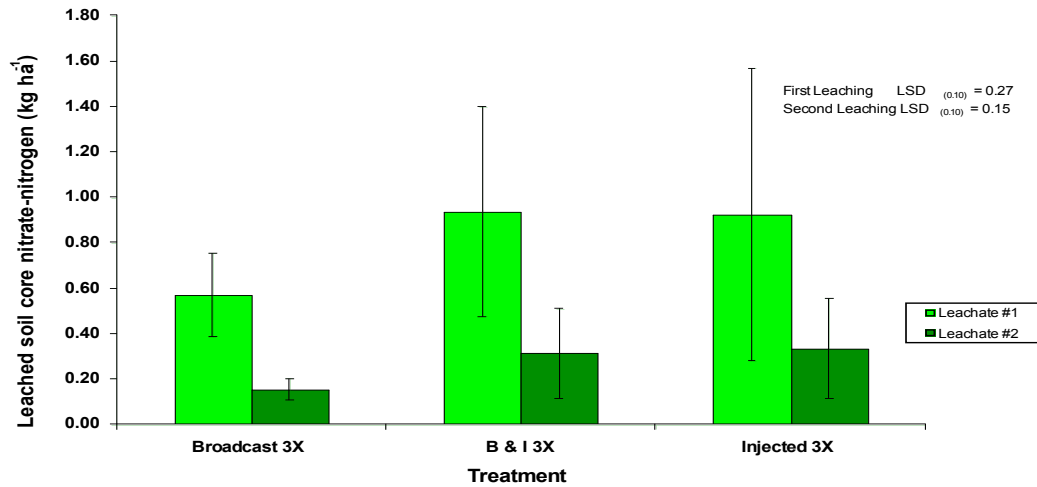


Figure 3.10 Dixon SCM site intact soil core leachate nitrate-nitrogen.

For orthophosphate in the leachate, the injected 3X manure treatment was found to result in more P for the first leaching (1.9 kg ha^{-1}) and the second leaching (1.5 kg ha^{-1}) than the broadcast 3X and broadcast and incorporated 3X manure treatments (Figure 3.11).

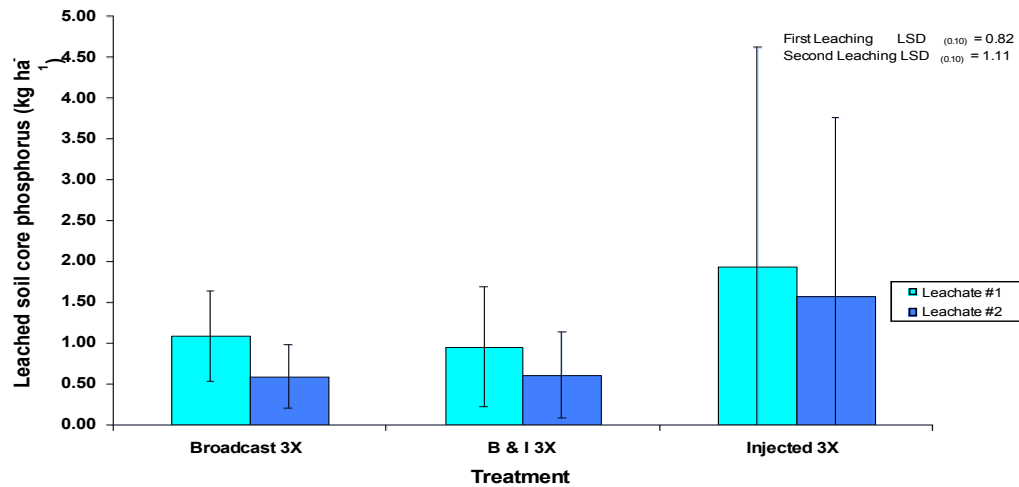


Figure 3.11 Dixon SCM site intact soil core leachate phosphorus.

Although not significantly higher in leachate $\text{NO}_3\text{-N}$ and P, due to high variability, the leachate $\text{NO}_3\text{-N}$ from the intact soil cores for the injected 3X and broadcast and incorporated 3X manure treatments was higher than the amount of leachate $\text{NO}_3\text{-N}$ measured in the broadcast 3X manure treatment for both leaching events. Leachate P for both leaching events in the intact soil cores was higher in the injected 3X treatment versus the broadcast 3X and broadcast and incorporated 3X manure treatments soil core leachate.

As with the thin section snowmelt runoff/leachate, the intact soil core water leachate follows a similar pattern in that the injected 3X manure treatment shows a higher pattern of leached TOC, TN, and P than the other two manure application treatments. Injected 3X water leachate $\text{NO}_3\text{-N}$ was similar to the broadcast and incorporated 3X treatment, but was still much higher than the broadcast 3X treatment.

4. Conclusions

More nutrient stratification was evident with broadcast cattle manure treatment compared to broadcast and incorporated, and injected application methods. The highest concentrations were found at the soil surface and then rapidly decreased with depth in the broadcast treatment while injection treatment showed higher levels of $\text{NO}_3\text{-N}$ and soil extractable P at the 5-10 cm depth. This distribution in injected manure applications would be expected to reduce nutrient export in surface water movement over frozen soils compared to surface placement. However, movement of nutrient in sub-surface water flow through the soil matrix in thawing or unfrozen soils could be increased by injection.

Thin sections removed from the field during the previous fall, and subjected to snowmelt under laboratory conditions showed that in the collected leachate and runoff, organic C and N and inorganic N and P were higher in the injected cattle manure treatment versus the broadcast and broadcast and incorporation treatments. It is evident that the placement of solid cattle manure in a cultivated field can affect nutrient distribution and potential transport, the effect of which will depend on the relative dominance of surface vs. sub-surface flow. The data from this study indicates that if sub-surface flow dominates, the placement of solid cattle manure via subsurface injection may contribute to greater amounts of transported TOC, TN and P.

4. Cited References

- Barker, B. 2007. Managing phosphorus based manure inputs. Top Crop Manager. December 2007. 33:
- Carefoot, J. P. and J.K. Whalen. 2003. Phosphorus concentrations in subsurface water as influenced by cropping systems and fertilizer sources. Can. J. Soil Sci. 83: 203–212.
- Gachter, R., J.M. Ngatiah and C. Stamm. 1998. Transport of phosphate from soil to surface waters by preferential flow. Environ. Sci. Technol. 32: 1865–1869.
- Hountin, J.A., A. Karam, D. Couillard^c and M. P. Cescas. 2000. Use of a fractionation procedure to assess the potential for P movement in a soil profile after 14 years of liquid pig manure fertilization . [Agric., Ecosystems & Environment](#). 78: 77-84.
- Lee, S.I., S.Y. Weon, C.W. Lee and B. Koopman. 2003. Removal of nitrogen and phosphate from wastewater by addition of bittern. Chemosphere. 51:265-271.
- Saskatchewan Soil Survey. 1989. Rural Municipality of Humboldt No. 370. Preliminary soil map and report. Saskatchewan Institute of Pedology, University of Saskatchewan, Saskatoon, SK, Canada.
- Simard, R. R., S. Beauchemin and P.M. Haygarth. 2000. Potential for preferential pathways of phosphorus transport. J. Environ. Qual. 29: 97–105.
- Toor, G.S., S. Hunger, J.D. Peak, J.T. Sims and D.L. Sparks. 2006. Advances in the characterization of phosphorus in organic wastes: environmental and agronomic applications. Advances in agronomy. 89: 1-72.
- Ulen, B and S. Snäll. 2007. Forms and retention of phosphorus in an illite-clay soil profile with a history of fertilisation with pig manure and mineral fertilizers. Geoderma. 137: 455–465.